ISSN 1318-0010
KZLTET 31(6)567(1997)

THE DIFFERENCE BETWEEN THE MAGNETO-CRYSTALLINE ANISOTROPY OF THE INTERMETALLIC ALLOY $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ AND INTERSTITIALLY MODIFIED $Pr_2(Co_{0.5}Fe_{0.5})_{17}N_{3-\delta}$

RAZLIKA MED MAGNETNO KRISTALNO ANIZOTROPIJO $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ IN $Pr_2(Co_{0.5}Fe_{0.5})_{17}N_{3-\delta}$

MATEJ KOMELJ, S. KOBE

Institut Jožef Stefan Jamova 39, 1000 Ljubljana, Slovenija

Prejem rokopisa - received: 1997-10-01; sprejem za objavo - accepted for publication: 1997-10-21

The alloy with the composition $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ has an easy-axis magneto-crystalline anisotropy. The anisotropy is changed to the easy-plane by introducing nitrogen on interstitial sites. We proved the difference between the anisotropy of the basic alloy and the nitrided composition directly by the magnetic measurements and by observing the domain structure by means of optical and magnetic force microscopy. The transition from one to another type of anisotropy can be explained by a simple model based on crystal structure and shape of the electronic cloud of the Pr ion.

Key words: permanent magnet materials, magneto crstalline anisotropy, nitriding

Intermetalna zlitina $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ ima osno magneto-kristalno anizotropijo. Z uvajanjem dušika na intersticijska mesta anizotropija preide v ravninsko. Razliko med tipoma anizotropij med obema spojinama dokažemo neposredno z magnetnimi meritvami in opazovanjem domenske strukture z mikroskopom na magnetno silo (MFM). Prehod iz ene anizotropije v drugo kot posledico spremenjene sestave lahko razložimo s preprostim modelom, ki temelji na kristalni strukturi in obliki elektronskega oblaka iona Pr.

Ključne besede: trajno-magnetni materiali, magneto-kristalna anizotropija, nitriranje

1 INTRODUCTION

It is well known that R_2T_{17}, where R stands for a rare earth and T for a transition metal, intermetallics exhibit interesting magnetic properties and represent important permanent magnet material[1]. To obtain high coercivity of the magnet it is necessary that the material has an easy-axis magneto-crystalline anisotropy and that the value of the coefficient K_1, which is a measure for the energy of the magneto-crystalline anisotropy, is as high as possible[2]. The magneto-crystalline anisotropy of the basic compound can be influenced by introducing nitrogen on interstitial sites in the crystal lattice[3]. The $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ compound crystallizes in the rhombohedral Th_2Zn_{17} type structure and it has easy-axis magneto-crystalline anisotropy[4,5]. But the anisotropy is too weak and the magnet based on this material does not exhibit desired properties. In our work we studied the influence of nitrogen in the $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ alloy. In Sm_2Fe_{17} intermetallic alloy the magnetic properties were successfully improved by introducing nitrogen to the interstitial sites of the crystal lattice[6].

2 EXPERIMENTAL

The samples were prepared from 99.9% pure elements by arc melting. Excess of Pr was added to a nominal composition to offset Pr evaporation losses during melting. After the fourth melting the samples were wrapped in a Ta foil and encapsulated after evacuation in quartz tubes and then annealed at 1000°C for 24 hours. Before and after the heat treatment their phase purity was determined by JEOL JXA 840 SEM/EPMA electron probe microanalysis. Nitriding, as a gas-solid reaction, was performed at 450°C for 10 hours in a high purity N_2 1 bar gas atmosphere. The nitriding temperature was previously determined by using DTA/TGA facilities (Netzch). The parent alloy and the nitrided powder were characterized by XRD. The magnetization measurements on the powdered and aligned samples were provided by the magnetometer-susceptometer (Manics) based on the Faraday principle. Magnetic domains were examined by magnetic force microscopy (MFM) using a Dimension 3000 scanning probe microscope (Digital Instruments, Inc.), which allows separate atomic force and magnetic force images to be collected in the course of one scan. Surface topography was obtained using Tapping Mode[7] AFM. High resolution MFM image was obtained by using Lift Mode software[7] and the ultra-soft $Fe\text{-}SiO_2$ tip. Images of the domain patterns were previously taken by Kerr microscopy using a Nikkon Optiphot XP-2 polarizing light microscope with a 150W Xe lamp.

3 RESULTS OF THE MEASUREMENTS

The magnetization versus applied field curves of the $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ bonded powder measured parallel and perpendicular to the direction of the alignment are shown in **Figure 1**. From these curves it is evident that the anisotropy field is greater then 30 kA/cm which implies the existence of weak easy-axis magneto-crystalline anisotropy. The domain pattern of this alloy, observed by optical microscope in a polarized light using the magneto-optic Kerr effect is shown in **Figure 2**. A star shaped or "labyrinth" pattern in the grains cut perpendicular to the c-axis and a banded or "strip" structure within the grains cut parallel to the c-axis are present. Such domain structure applies for materials with easy-axis type of magneto-crystalline anisotropy where the crystallographic c-axis defines the easy direction[8]. **Figure 3** shows the same area observed by the magnetic force microscope (MFM) which appears to be in a good agreement with Kerr microscopy. Both magnetization curves of the nitrided powder, measured parallel and perpendicular to the direction of the alignment are essentially the same (**Figure 4**) that means that the nitrided material does not have an easy-axis magneto-crystalline anisotropy. This fact was confirmed also by observation of the domain structure. **Figure 5** shows the Kerr image of a large (~100 μm) particle. Because of the slow nitrogen bulk diffusion[9] just a layer of width ~5 μm was nitrogenated. The core area represents the basic $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ material. The shell resolution is low, and no magnetic structure was observed in the nitrided layer. Only strip domains were found in the core region. On **Figure 6** is shown a MFM detail image of the core-shell border area of the same particle with a sharp demarcation between the strip domain pattern in the core area and the labyrinth domain structure in the nitrided shell with the star domain width of ~1-1.2 μm which is significant for easy-plane magneto-crystalline anisotropy[10].

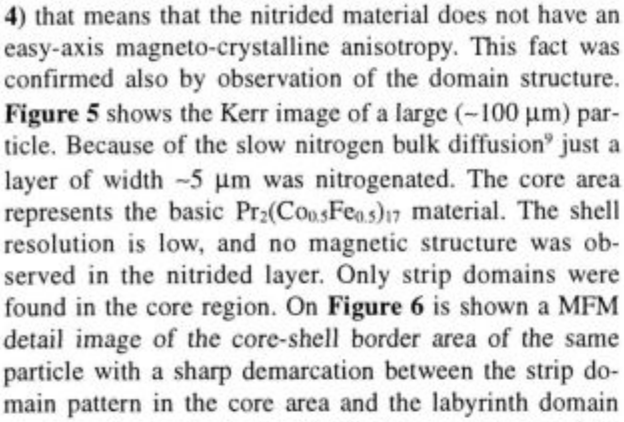

Figure 1: Magnetization versus applied field of the $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ bonded powder measured parallel (upper curve) and perpendicular (lower curve) to the direction of the aligment. The anisotropy field is greater then 30 kA/cm

Slika 1: Magnetizacija prašnega vzorca $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ v odvisnosti od zunanjega magnetnega polja merjena vzporedno (zgornja krivulja), in pravokotno (spodnja krivulja), glede na smer predhodne namagnetenosti prahu

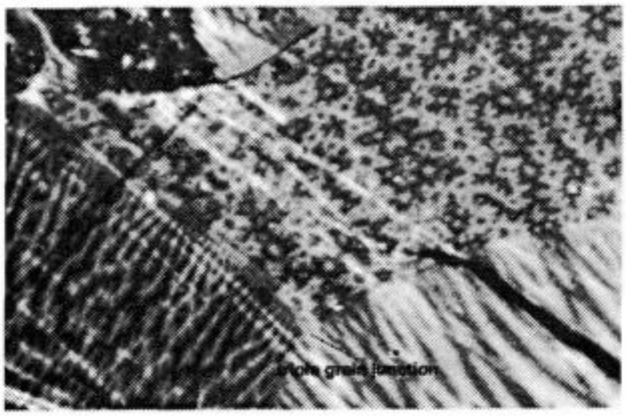

Figure 2: The domain pattern of the alloy $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ observed by optical microscope in a polarized light using magneto-optic Kerr effect. Star shaped or "labyrinth" pattern in grains cut perpendicular to the c-axis and a banded or "strip" structure within grains cut parallel to the c-axis are present

Slika 2: Domenska struktura zlitine $Pr_2(Co_{0.5}Fe_{0.5})_{17}$, opazovana z optičnim mikroskopom v polarizirani svetlobi s pomočjo Kerrovega efekta. V zrnih, odrezanih pravokotno glede na os c, vidimo labirintno strukturo domen zvezdaste oblike. V zrnih, ki so odrezana vzporedno z osjo c pa so črtaste domene v obliki pasov

4 THEORETICAL

Undesired transition from the easy-axis to the plane magneto-crystalline anisotropy due to the introduced nitrogen in the case of $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ contrary to the case of Sm_2Fe_{17} [6] can be explained in the frame of the simplified crystal field theory[11]. We assume that the energy of the magneto-crystalline anisotropy is given by the electrostatic interaction between the 4f charge distribution of the rare earth atom and the non-4f charges present in the

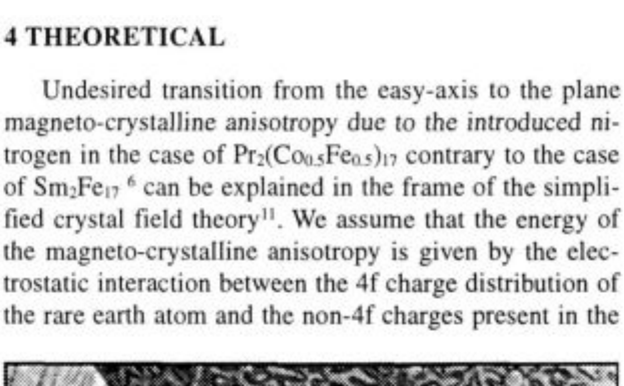

Figure 3: MFM image of the same area as in **Figure 2**

Slika 3: MFM posnetek istega območja kot na **sliki 2**

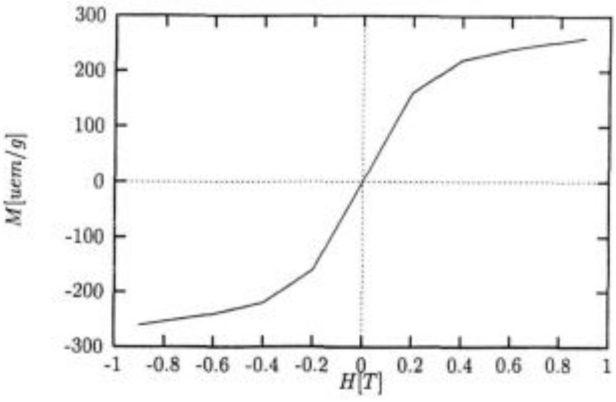

Figure 4: Magnetization curves of nitrided powder measured parallel, and perpendicular, to the direction of the alignment are the same

Slika 4: Krivulja magnetizacije nitriranega prahu, merjena pravokotno in vzporedno glede na smer predhodne namagnetenosti prahu

lattice. The change of the coefficient K_1 upon the interstitial modification in the first approximation depends:

- on the angle θ between the directions of the nitrogen atom and the magnetization relative to the position of the rare earth atom: **Figure 7**
- and to the quadrapole contribution n_2 to the 4f charge density.

One can schematically conclude that rare earth atoms with $n_2<0$ (Pr, Nd, Dy etc.) have the oblate shape of the 4f electron cloud while in the case of Sm with $n_2>0$ it can be described as a prolate. To estimate whether the K_1 is increased or decreased after the nitriding there is a simple rule[11]:

$$\mathrm{sgn}(\Delta K_1) = \mathrm{sgn}(n_2)\ \mathrm{sgn}(\theta)$$

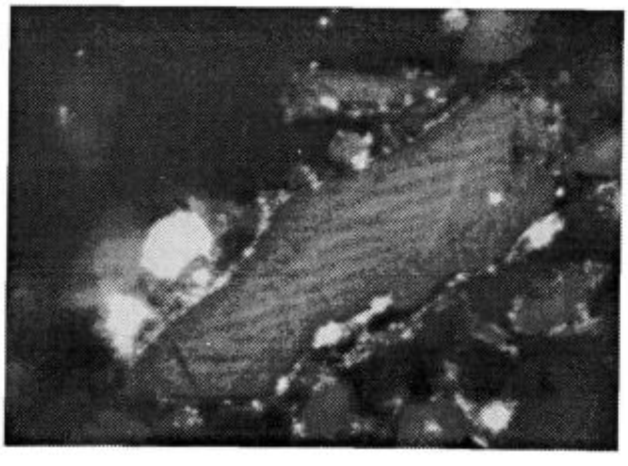

Figure 5: Kerr image of a large (~100 µm) particle. Just a layer of width ~5 µm was nitrogenated. The core area represents the basic $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ alloy

Slika 5: Posnetek velikega (~100 µm) delca s pomočjo Kerrovega efekta. Nitrirana je samo zunanja plast debeline ~5 µm. Jedro predstavlja osnovna zlitina $Pr_2(Co_{0.5}Fe_{0.5})_{17}$

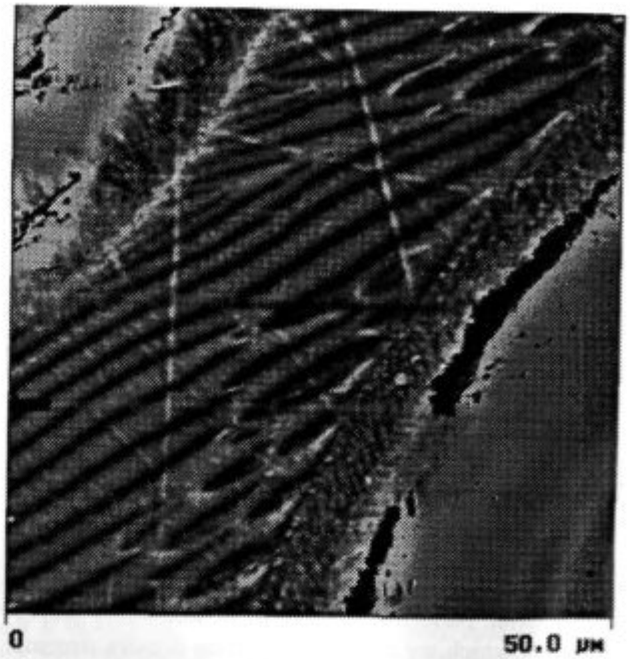

Figure 6: MFM detail image of the core-shell border of the same particle as in **Figure 5**. A sharp demarcation between the strip domain pattern in the corearea and the labyrinth domain structure in the nitrided shell is shown

Slika 6: MFM detajlni posnetek meje med nitriranim in nenitriranim območjem delca iz **slike 5**. Ostro se vidi razlika med črtastimi domenami v nenitriranem območju ter zvezdastimi domenami iz nitrirane plasti

where $\mathrm{sgn}(\theta = 0°) = -1$ and $\mathrm{sgn}(\theta = 90°) = 1$. It implies that in the case of Pr ($n_2<0$) we have to look for interstitial sites with the axial coordination ($\theta = 0°$) which is not the case for the site 9e in Th_2Zn_{17} type of crystal structure. It has in-plane interstitial coordination ($\theta = 90°$) which is favorable for the Sm ($n_2>0$) based materials.

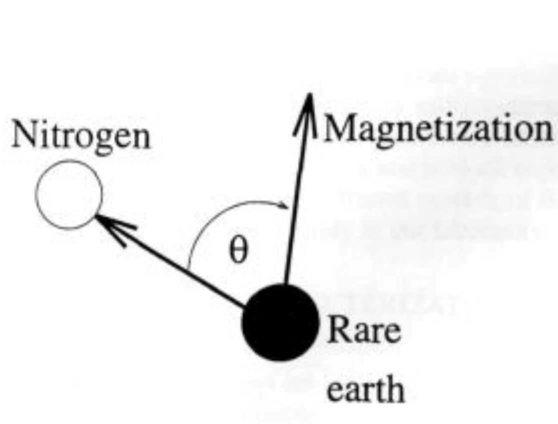

Figure 7: Angle θ between the directions of the nitrogen atom and the magnetization relative to the position of rare earth atom

Slika 7: Kot θ med zveznico atoma dušika ter atoma redke zemlje in smerjo magnetizacije

5 CONCLUSION

It was shown that besides the magneto-optic Kerr effect MFM can be used as an important technique for rapid and simple characterization of the magnetic structure of new magnetic materials. When the magnetic structure is too fine for optical microscopy, MFM can serve as a very convenient method in observing and characterizing the magnetic structure of different and unknown magnetic materials. After the successful interstitial modification of the Sm_2Fe_{17} [3,6] and some other intermetallics[3] it was hoped that the same procedure could be applied also to the $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ alloy. Instead of the increasing of magneto-crystalline anisotropy even a transition from the easy-axis to the undesired easy-plane type was observed. Therefore the nitrided alloy $Pr_2(Co_{0.5}Fe_{0.5})_{17}$ can not be used as a permanent magnet material. Nevertheless it has very interesting properties from which we can learn much on domain structure and the effects of nitriding. Finally the experimental results obtained on the investigated alloy agree with the predictions of a model based on a crystal field theory[11].

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